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Heat and Mass Transfer Effects in a Furnace-Based Micropyrolyzer

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Abstract

Microgram-scale reactors combined with gas chromatography (GC) coupled to mass spectrometry (MS) or flame ionization detection (FID) are used widely in pyrolysis research. Whether these devices meet the expected fast heating rates and short vapor residence times of fast pyrolysis have not been verified. In this study, experiments and simulations are used to investigate heat and mass transfer in a furnace-based micropyrolyzer. Surprisingly, heating rates obtained from the temperature history of sample cups in the reactor were modest compared to the greater than 1000 K s⁻¹ heating rates sometimes assumed for such reactors. The heating rate at 773 K, employed commonly in fast pyrolysis, was only 180 K s⁻¹. The highest rate observed was 494 K s⁻¹ at a furnace temperature of 1268 K, which is well above typical pyrolysis temperatures. The mass transfer of volatilized samples was studied using both an optically accessible furnace and computational fluid dynamics. The standard sample cups used with these micropyrolyzers impede the escape of vapors. The use of shallow perforated cups overcame this mass transfer limitation to lead to levoglucosan yields $\approx 10\%$ higher than usually reported for the pyrolysis of cellulose.

Disciplines

Heat Transfer, Combustion | Mechanical Engineering

Comments

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Heat and Mass Transfer Effects in a Furnace-Based Micropyrolyzer

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Abstract: Microgram-scale reactors combined with GC-MS or FID have found wide use in pyrolysis research. Whether these devices meet expected fast heating rates and short vapor residence times of fast-pyrolysis have not been verified. In this paper, experiments and simulations are used to investigate heat and mass transfer in a furnace-based micropyrolyzer. Surprisingly, heating rates obtained from the temperature history of sample cups in the reactor were modest compared to the greater than 1000 Ks⁻¹ heating rates sometimes assumed for such reactors. The heating rate at 773 K, commonly employed in fast pyrolysis was only 180 Ks⁻¹. The highest rate observed was 494 Ks⁻¹ at a furnace temperature of 1268 K, which is well above typical pyrolysis temperatures. Mass transfer of volatilized samples was studied using both an optically accessible furnace and computational fluid dynamics. It was found that the standard sample cups used with these micropyrolyzers impede escape of vapors. Use of shallow perforated cups overcame this mass transfer limitation, achieving levoglucosan yields ≈10% higher than usually reported for pyrolysis of cellulose.

Introduction

Microgram-scale pyrolysis reactors in combination with GC-MS or GC-FID have found wide use in recent years to study fast pyrolysis. The advantages of these so-called Py-GC systems include their relative simplicity, reproducibility of results, opportunities to use them in high throughput screening and, with careful attention to sample handling and calibration of the GC, good mass closures.

The importance of performing biomass pyrolysis experiments under conditions that avoid heat and mass transfer limitations are well understood.^[1,2] If a sample is heated too slowly, low activation energy, char-forming reactions dominate, resulting in low yields of liquids.^[3,4] Since the reactions that produce volatile products have higher activation energies, high heat fluxes are important for rapidly reaching temperatures high enough for these reactions to dominate.^[5,6] Also, if vapor products are transported away from the reaction zone too slowly, they can polymerize to non-volatile

secondary products that eventually dehydrate to char.^[7] For this reason, fast pyrolysis reactors are usually ventilated with inert or recirculated gases to rapidly transport vapors out of the reaction zone.

Heat and mass transfer issues become even more critical if micropyrolyzers are employed in chemical kinetic studies of pyrolysis. Unless sample heating is much faster than the reactions under investigation, a significant non-isothermal effect is introduced into the time evolution of chemical species. Mass transfer limitations can affect chemical kinetic measurements in two ways. The first is simply a delay in response to the evolution of chemical species if these are swept too slowly from reactor to detector. The second effect occurs if there is a significant delay in the time it takes volatile products to diffuse out of a sample holder into the ventilating gas stream.

Whether these heat and mass transfer effects are significant in Py-GC systems has received little attention. The manufacturers of micropyrolyzers claim very high heating rates, exceeding 1000 Ks⁻¹.^[8,9] They suggest that sample masses be no larger than 0.2–0.5 mg to avoid mass transfer limitations. We have found only one paper that discusses the effect of heating rate and only two papers that evaluate mass transfer effects in micropyrolyzers.^[10–12]

Zhan et al.^[10] calculated that heat transfer effects are small for cellulose samples smaller than 0.8 mg. Hosaka et al.^[11] speculated that the head space of sample cups used in furnace-based micropyrolyzers can trap pyrolysis vapors although this concern was not supported by experiments or computational analysis. In an effort to overcome this potential problem, a perforated cup containing a plug of quartz wool to support the sample was introduced. Unfortunately, this plug introduces its own heat and mass transfer challenges, reducing the rate of heat conduction to the sample from the bottom of the cup and imposing an unknown flow resistance through the perforated cup. Patwardhan et al.^[12] in a study of cellulose pyrolysis in a furnace-based micropyrolyzer evaluated the effect of sample weight on product yields. For pyrolysis at 773 K they found no effect for samples in the mass range of 0.2 – 0.8 mg although larger samples introduced mass transfer limitations.

In this paper we investigate heat and mass transfer in a furnace-based micropyrolysis system. Heating rates of sample cups were measured with miniature thermocouples while heating rates of biomass samples in sample cups were simulated using detailed Finite Element Analysis (FEA). Mass transfer from sample cups were visualized with an optically accessible furnace and simulated with a Computational Fluid Dynamics (CFD) model.

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Results and Discussion

The experiments were performed in either a micropyrolyzer (Frontier, EGA/PY-3030D or EGA/PY-2020D) integrated with a GC-FID or using a custom-built, optically accessible furnace for visual observations of vapor transport. Biomass samples were held in 3.95 mm dia. stainless steel cups from Frontier Labs, which were inserted into the furnace section of the pyrolyzer attached to the end of a stainless steel hook. Both shallow (5 mm) and deep (8 mm) cups were tested. Some experiments employed intact cups while others used perforated cups. A few experiments did not use cups but instead coated samples directly onto the hook. Additionally, exposed thermocouple beads were directly inserted in the furnace to measure heating rates. It is important to note that the cups, which set on an annular ledge within the furnace, were exposed to heat transfer through the combined mechanisms of conduction, convection, and radiation. Only radiation and convection contribute to heating of the sample hook and thermocouple bead since they did not come in contact with the ledge. Additional details are presented in the experimental section of the paper.

Heating Rates in Micropyrolyzer Samples

Two configurations, an exposed bead thermocouple and a thermocouple spot welded to the floor of a deep cup were used to measure temperature evolution inside the micropyrolyzer from which heating rates as functions of furnace wall temperature were determined. As shown in Figure 1, for furnace temperatures in the range of 573 - 1268 K, the heating rates were 100 - 750 Ks⁻¹ for the exposed bead but only 100 - 495 Ks⁻¹ for the intact deep cup. Although these are much higher than achieved in thermogravimetric analyzers (<3 Ks⁻¹) frequently used to study pyrolysis, they fall short of the 1000 Ks⁻¹ heating rates sometimes thought important to fast pyrolysis.^[13,14] Heating rates will be even slower for biomass within a sample cup, as subsequently demonstrated.

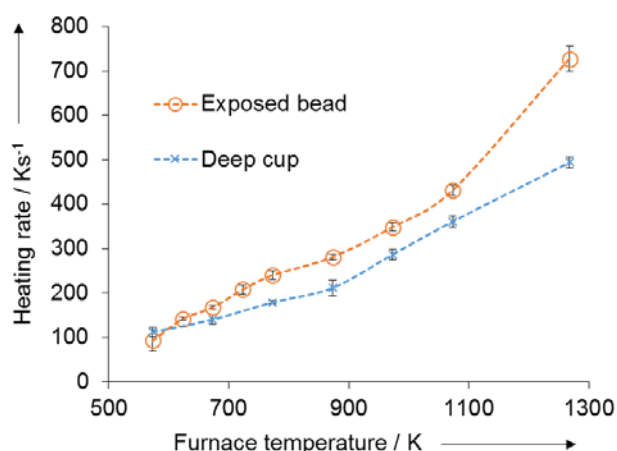


Figure 1. Heating rates for an exposed bead thermocouple and a deep cup in the micropyrolyzer furnace (Error bars are one standard deviation in each direction from the average value).

Using experimental data and FEA simulations, the heating rate of an intact deep cup inside a micropyrolyzer was calculated for 673, 773 and 873 K furnace temperatures. Moreover, from the simulated results, the relative contribution of various heat transfer modes was determined. Figure 2 shows good agreement between the total heating rates calculated from experiments and simulations. Conduction is the major contributor of heating rate closely followed by convection with only a small contribution from radiation. As might be expected, conduction supported a larger heat flux than convection even though the surface area of the cup exposed to gas flow (190 mm²) is much larger than the contact surface area between the tube and the cup (<1 mm²) where conduction occurs.

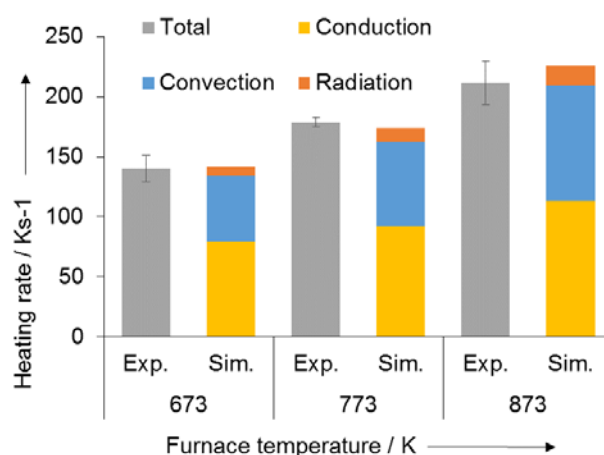


Figure 2. Heating rates for an empty intact deep cup heated in a micropyrolyzer. The columns show overall heating rate as measured experimentally (Exp.) and the relative contribution for various heat transfer modes as calculated from simulation (Sim.). (Error bars are one standard deviation in each direction from the average value).

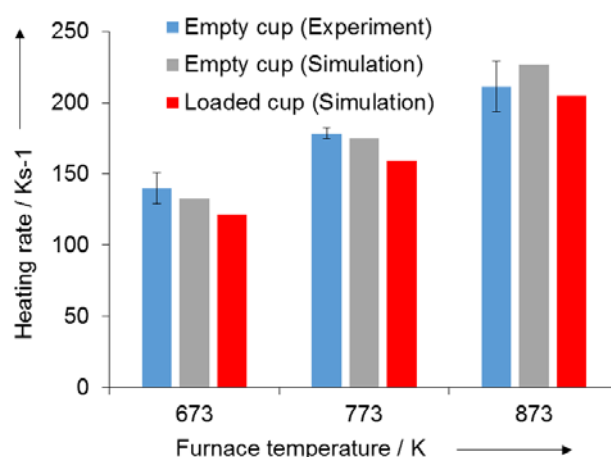


Figure 3. Heating rates for an empty intact deep cup (both Simulated and Experiment) and loaded with a 500 µg cellulose sample (Simulated) inside a micropyrolyzer. (Error bars are one standard deviation in each direction from the average value).

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Although we were not able to directly measure the temperature of biomass in the sample cups, we were able to simulate the heating of biomass in the cups. Figure 3 compares the simulations of heating rate for a 500 μg sample of cellulose in a deep cup to the sample cup alone for various furnace temperatures. The heating rate of the biomass is only about 10% slower than for the cup itself. Figure 3 also compares the measured heating rate for the empty sample cup, which is within 10% of the simulated heating rate.

Mass Transfer Inside Sample Holders

The volatilization of iodine crystals from a glass sample cup within an optically accessible furnace is shown in Figure 4. Images a and b are for a deep cup immediately after insertion into the furnace and twenty seconds later, respectively. Images c and d are for a shallow cup immediately after insertion into the furnace and five seconds later, respectively. Both true color and black and white images are included to help visualize volatilization of the purple iodine vapors. As can be seen, the deep cup generates a persistent cloud of iodine vapors and even deposition of iodine crystals near the top of the cup whereas the shallow cup readily disperses the iodine vapor. During the test, there was no visual evidence of carrier gas penetrating the cup and entraining the volatilized products. Based on visual observations, iodine was evacuated from the furnace zone in 10 s for the shallow cup while it took up to 85 s for the deep cup. This suggests that mass transfer may introduce limitations when using the deep cups commonly employed in experiments with furnace-type micropyrolyzers.

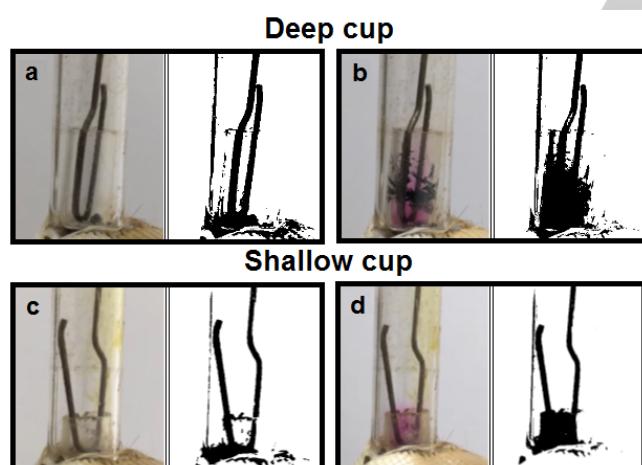


Figure 4. Iodine volatilization at 620 K illustrating vapor hold-up in sample cups: (a) deep cup at 0 s; (b) deep cup at 20 s; (c) shallow cup at 0 s; (d) shallow cup at 5 s. Dark purple and black show the presence of gases inside the cups. For both cups the majority of their inner volume was occupied by iodine gas until late in the experiments, indicating stagnation of produced gases.

CFD simulations of velocity fields around different sample holders in the furnace are shown in Figure 5. The dark blue areas represent zones of stagnation flow. Only the hook sample holder is free of such stagnation in the vicinity of the hook. Even the perforated cups show stagnation regions close to the sample location in the bottom of the cup although they are much smaller than for the intact cups.

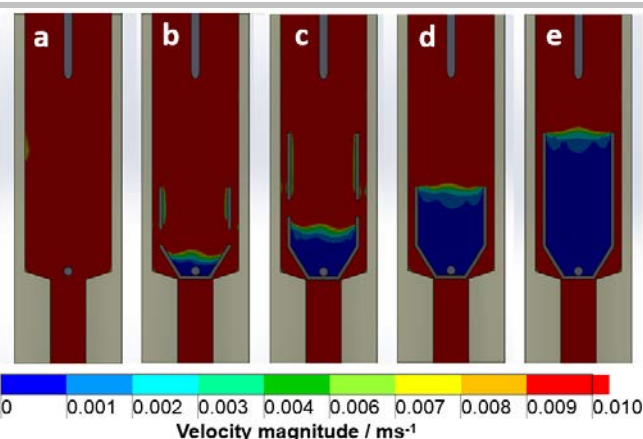


Figure 5. Flow of carrier gas around sample holders inside the micropyrolyzer. The color contours show the distribution of the gas velocity magnitude along the centerline of a vertical plane through the furnace. (a) hook, (b) perforated shallow cup, (c) perforated deep cup (UV accessible), (d) intact shallow cup, and (e) intact deep cup. Decrease in height of the low velocity region (dark blue) is evident in the modified sample holders (a-c).

As expected, higher velocities close to the sample location promote advection of volatiles away from the sample. Using representative free stream velocities near the location of the sample, dimensionless Péclet numbers (Pe) were calculated based on naphthalene vapor transported through helium gas to quantify differences in heat and mass transport (Table 1). Péclet number was approximately unity for the hook, indicating strong advection during transport of volatiles from the sample. Conversely, the intact cups have $Pe \approx 0.01$ indicating the dominance of diffusion, which is not readily overcome by simply increasing the ventilation rate through the micropyrolyzer. The perforated cups are intermediate with $Pe \approx 0.1$, indicating contributions from both diffusion and advection.

Table 1. Péclet number (Pe) calculated for mass transport for sample holders. Advection characteristic length (L_c) and velocity (v_m) where obtained from CFD simulation results shown in Figure 5. The binary diffusion coefficient for helium and naphthalene is $D_{AB} = 5.15 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$.^[15]

Sample holder	L_c (mm)	v_m (ms^{-1})	Pe
Hook	0.5	0.1400	1.304
Shallow perforated cup	2.3	0.0020	0.089
Deep perforated cup	2.3	0.0020	0.089
Deep perforated cup UV	3.9	0.0010	0.076
Deep intact cup	8.0	0.0001	0.016
Shallow intact cup	5.0	0.0001	0.010

Time Constants for Evolution of Vapors from Sample Holders During Rapid Heating

The time evolution of naphthalene vapors from the micropyrolyzer for different sample holders was evaluated by directly connecting the furnace outlet to a FID detector. As shown in Figure 6, considerable differences in the characteristic time constant for this evolution is evident among the different sample holders. Coating a sample hook with naphthalene or using perforated cups to hold the sample produced relatively short time constants for mass transfer (≈ 0.2 s). Both shallow and deep cups that were perforated displayed time constants that were only slightly longer than for the hook, suggesting that the time constant is due mostly

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to the transport time of vapors from the furnace to the FID.^[16] On the other hand, intact deep cups had time constants approaching 1.75 s. These results are consistent with experimental results of Fig. 4 and simulation results of Fig. 5.

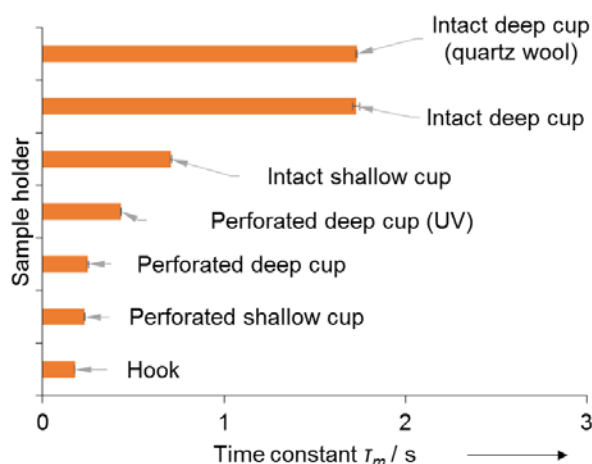


Figure 6. Time constant for multiple sample holders characterizing the evolution of volatile naphthalene when heated in the micropyrolyzer (Error bars show one standard deviation to each direction from the mean value).

The impact of the choice of sample holder during actual pyrolysis experiments is illustrated in Fig. 7. An approximately 500 μg sample of cellulose was pyrolyzed at 673 K in both an intact deep cup and a perforated shallow cup. Levoglucosan yield was almost 10% greater in the perforated shallow cup.

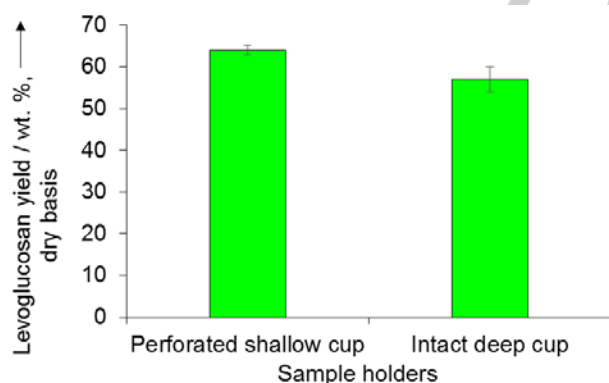


Figure 7. Levoglucosan yield from powdered cellulose pyrolysis at 673K furnace temperature. Perforated shallow cup outperformed the benchmark intact deep cup (Error bars show one standard deviation to each direction from the mean value).

Conclusions

Experiments and simulations provided information on heat and mass transfer limitations in furnace-based micropyrolyzers. The maximum heating rate for the intact deep sample cup often used with these micropyrolyzers was only about 495 K s^{-1} , considerably slower than the 1000 K s^{-1} sometimes assumed for these systems. Nevertheless, this heating rate is about two orders of magnitude faster than attained in thermogravimetric analyzers, which are sometimes employed in pyrolysis studies. It is probably fast enough to represent heating rates in fluidized bed and auger pyrolyzers.

Experiments and simulations determined that diffusion from the interior of sample cups limited mass transfer rates when using intact deep cups. Substitution of hooks and shallow or perforated cups significantly reduced the time constant for mass transfer, which was likely limited by gas advection from furnace to detector.

Experimental Section

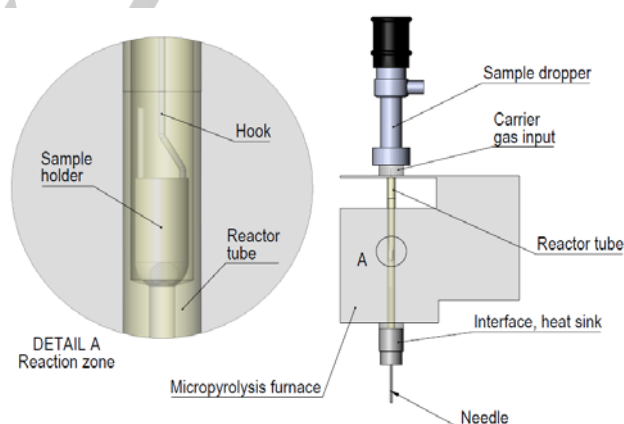


Figure 8. Schematics of EGA/PY 3030D Frontier Micropyrolyzer. Sample holder is inserted into the reactor tube.

Pyrolysis System

Most experiments were performed in a Frontier EGA/PY 3030D Micropyrolyzer, which consists of a sample dropper, a quartz or stainless steel reactor tube, a furnace section, and an interface to transfer pyrolysis vapors to appropriate analytical instrumentation for on-line analysis (see Fig. 8). The hooked end of a stainless steel wire is pressed into a sample cup while the other end is held by a sample dropper, which allows the cup to be suspended in the top of the reactor tube. Once the furnace is preheated to the desired pyrolysis temperature, the sample dropper releases the end of the hooked wire, allowing the cup to fall into the center of the furnace section where it lands upon an annular ledge formed from the sudden contraction in the reactor tube diameter. It remains at this position near the center of the furnace section for the duration of the experiment. Helium carrier gas flows into the top of the reactor tube, entrains vapors released from samples contained in the cup, and exits the reactor tube through a needle attached to the bottom of interface, which directs the

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vapors into appropriate on-line analytical instrumentation subsequently described. The effect of a variety of sample holders on mass transfer of volatile products was evaluated. Figure 9 illustrates the several kinds of sample cups evaluated, all constructed of 0.2 mm thick stainless steel with diameters of 3.95 mm. Cups were either 5 mm deep (Frontier, PY1-EC50F), referred to as shallow cups, or 8 mm deep (Frontier, PY1-EC80F), referred to as deep cups. The walls of these cups were either intact or contained circular perforations on two sides, which were intended to enhance transport of vapors from the cups. Other cups were ultraviolet radiation-accessible perforated deep cups (Frontier, PY1-EC80UV) which are referred to as "UV" cups. Notice in Fig. 9 that the sample hook used to hold the sample cup in the furnace was also improvised as a sample holder, which was either dipped into melted or slurried samples to form a film at the bottom of the hook.

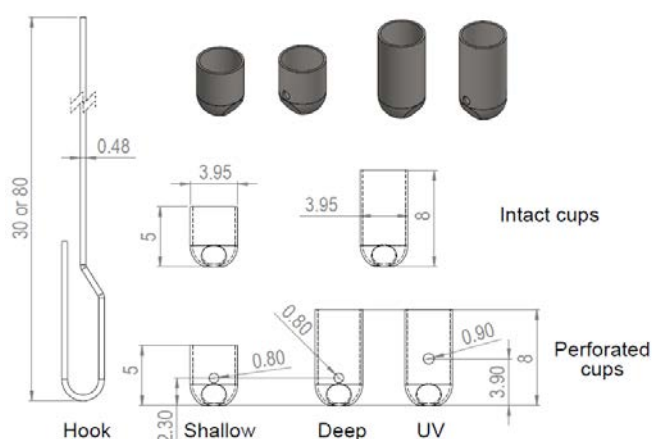


Figure 9. Sample holders evaluated in this study. All dimensions in mm.

A few experiments were performed in a modified micropyrolyzer that excluded the surrounding furnace. Its absence allowed optical access to the sample holder. To provide heat to the pyrolyzer, the furnace was replaced with heat cable (Briskheat, 120 VAC/ 25 W/ 6in heat cable) wrapped around the bottom half of the quartz tube below the reaction zone. The temperature of the cable was kept at 573 K by a controller (Digi-Sense, 36225 62). Helium carrier gas flowed through the reactor tube at 100 ml/min. Diffusion of vapors from 0.5 mm thick shallow and deep glass cups (Frontier, PY1-EC50GQ) was visualized by using iodine crystals as the samples, which has low boiling point (458 K) and produces purple vapors.^[17] The sample cups were loaded with 300 μ g of iodine and dropped into the preheated furnace section for 10 min. Experiments were video recorded, and selected frames were enhanced using functions Binarize and Colorize in Wolfram Mathematica 10.2.

Heating rates in the furnace section of the micropyrolyzer were measured with type K thin-wire thermocouples. In some experiments a stainless steel thermocouple bead of 200 μ m diameter and 30 μ g mass (Omega, KMQSS-010E-6) was attached to the sample hook such that the bead was suspended in the center of the curved section of the sample hook, allowing it to be easily inserted into the center of the furnace section (see Fig. 10). For other experiments a pair of fine thermocouple wires (Omega, CHAL-010-BW) were spot welded onto the floor of a deep cup to form a couple. The wires passed out of through a two-bore ceramic tube which prevented the wires from contacting one another as they passed out of the furnace (see Fig. 10). The temperatures measured from each of these thermocouple configurations were recorded with a National Instruments thermocouple meter (USB-TC01). The heating rate was calculated by dividing the difference between the initial temperature and 90% of the final temperature by the time needed to achieve the latter temperature. The characteristic time constant for heating was based on the assumption of a first order thermal response.^[18]

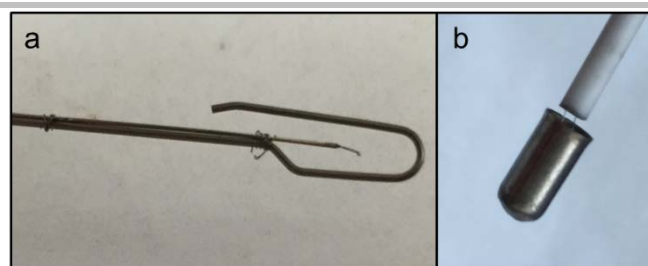


Figure 10. Thermocouple configurations. (a) Thermocouple bead fixed to sample hook; (b) thermocouple wires spot welded to floor of sample cup.

A GC-FID (Bruker, 430 GC) installed with a Phenomenex ZB-1701 capillary column was used for quantitative analysis of levoglucosan from cellulose in a few experiments. Sigmacell Type 50 cellulose (Sigma-Aldrich) in the amount of 500 ± 10 μ g was pyrolyzed at 673 K. The GC-FID was calibrated with aqueous solutions of levoglucosan (Carbosynth, ML06636) for expected yields in the range of 10–80 wt. % dry cellulose basis. The reactor temperature was chosen to match temperatures that achieve maximum levoglucosan yield^[19] or exceed the 658 K boiling point of levoglucosan.^[20] The reactor-to-GC interface, and the split valve were kept at 673 K to prevent undesired condensation of products. The helium flow rate was 100 ml/min. The split ratio was 100:1.

Since the GC did not allow dynamic measurements of volatile release from the sample cups, for some experiments the GC was replaced with a 500 mm long deactivated column without a stationary phase (Agilent Technologies, 160-2845-5) for the purpose of rapidly moving product vapors from the micropyrolyzer to the FID (Varian, CP-3800). For these experiments approximately 400 μ g of naphthalene was inserted into a sample cup as solid or coated onto the sample hook as a liquid that solidified. The furnace set point was 573 K, well above the 490 K boiling point of naphthalene^[17] to assure its rapid melting and evaporation. Helium sweep gas was set to 100 ml/min. The signal from the FID was recorded every 0.1 s over a 300 s test duration. An example of the response curve is illustrated in Fig. 11. The decay portion of the response curve was analyzed as a first order dynamic system to obtain a time constant associated with the transport of volatilized naphthalene from the sample holder to the FID.

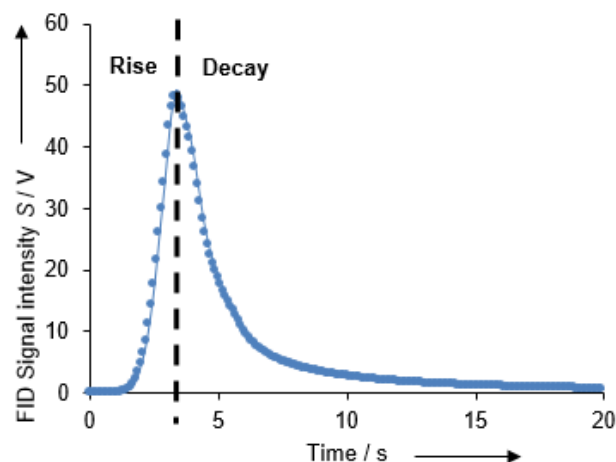


Figure 11. Example of FID signal from volatilization of naphthalene from a sample cup in the micropyrolyzer. Decay and rise sections are shown divided by vertical line coincident to the maximum signal.

Solidworks Flow Simulation 2015 was used to develop a finite element analysis (FEA) model of the micropyrolyzer and simulate transient heating of a deep metallic cup, both empty and containing 500 μ g of cellulose at furnace temperatures of 673, 773, and 873 K. The model included

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convection, conduction, and radiation heat transfer from the furnace to the sample cup. Contact resistance under light mechanical loads between the ledge of the reactor tube and the cup was estimated to be $3.7 \times 10^{-4} \text{ m}^2 \text{KW}^{-1}$ ^[21] and between the cup and the biomass sample was estimated to be $6.14 \times 10^{-4} \text{ m}^2 \text{KW}^{-1}$.^[22] The helium gas flow rate was assumed to be 100 ml/min.

Solidworks Flow Simulation 2015 was also used to develop a computational fluid dynamic (CFD) model of gas transport through the micropyrolyzer. The input flow rate was 100 ml/min at standard conditions. The experimental operating conditions of the micropyrolyzer are pressure of 207 kPa and furnace temperature set to 673 K.^[23] Péclet number^[24] was calculated to compare advection to diffusion of naphthalene through the system. The binary diffusivity constant for naphthalene in helium was obtained from the equation proposed by Fuller et al.^[15] Representative free stream velocity magnitude values of the carrier gas around the holder were used to estimate Pe. For the FEA and CFD analyses, a summary of boundary conditions, thermal properties of substances, details of the simulations and post-processing of results are in Appendix A.^[18,21,22,25–35]

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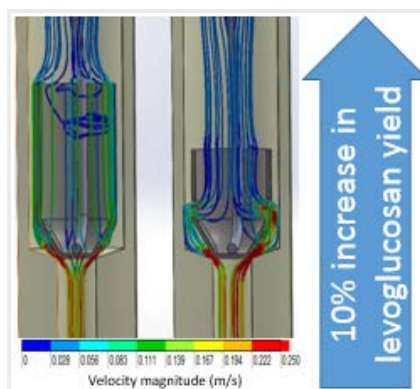
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Keywords: Pyrolysis • Heating rate • Simulation • Heat and mass transfer • Levoglucosan

- [1] A. Pandey, T. Bhaskar, M. Stöcker, R. Sukumaran, *Recent Advances in Thermochemical Conversion of Biomass*, Elsevier Science, **2015**.
- [2] G. Maschio, A. Lucchesi, C. Koufopoulos, in *Adv. Thermochem. Biomass Convers.*, Springer, **1993**, pp. 746–759.
- [3] F. Shafizadeh, in *Symp. Math. Model. Biomass Pyrolysis Phenom.*, ACS Division Of Fuel Chemistry, Preprints, Washington DC, **1983**, pp. 285–290.
- [4] O. Boutin, M. Ferrer, J. Lédé, *J. Anal. Appl. Pyrolysis* **1998**, *47*, 13–31.
- [5] V. Kothari, M. J. Antal, *Fuel* **1985**, *64*, 1487–1494.
- [6] T. Reed, C. Cowdery, *ACS Annu. Meet.* **1987**, *1987*, 68–81.
- [7] M. J. J. Antal, G. Varhegyi, *Ind. Eng. Chem. Res.* **1995**, *34*, 703–717.
- [8] Frontier Laboratories Ltd., *Multi-Shot Pyrolyzer EGA/PY-3030D, Operation Manual*, Frontier Laboratories Ltd., **n.d.**
- [9] Frontier Laboratories Ltd., *Double-Shot Pyrolyzer PY-2020iD, Operation Manual*, Frontier Laboratories Ltd., **n.d.**
- [10] J. Zhang, M. W. Nolte, B. H. Shanks, *ACS Sustain. Chem. Eng.* **2014**, *2*, 2820–2830.
- [11] A. Hosaka, C. Watanabe, S. Tsuge, *J. Anal. Appl. Pyrolysis* **2007**, *78*, 452–455.
- [12] P. R. Patwardhan, J. A. Satrio, R. C. Brown, B. H. Shanks, *J. Anal. Appl. Pyrolysis* **2009**, *86*, 323–330.
- [13] P. Basu, *Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory*, Elsevier Science, **2013**.
- [14] A. V. Bridgwater, *J. Anal. Appl. Pyrolysis* **1999**, *51*, 3–22.
- [15] A. P. Sinha, P. De, *Mass Transfer: Principles and Operations*, PHI Learning Pvt. Ltd., **2012**.
- [16] O. Levenspiel, *Chemical Reaction Engineering*, **1999**.
- [17] R. Perry, D. Green, J. Maloney, *Perry's Chemical Engineers' Handbook*, **1997**.
- [18] Y. a. Cengel, S. Klein, W. Beckman, **2002**, 896.
- [19] X. Zhou, M. W. Nolte, B. H. Shanks, L. J. Broadbelt, *Ind. Eng. Chem. Res.* **2014**, *53*, 13290–13301.
- [20] T. Shoji, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **2014**, *109*, 185–195.
- [21] S. Song, M. M. Yovanovich, F. O. Goodman, *J. Heat Transfer* **1993**, *115*, 533–540.
- [22] M. Bahrami, J. R. Culham, M. M. Yovanovich, *J. Heat Transf.* **2004**, *126*, 896–905.
- [23] K. H. Kim, X. Bai, R. C. Brown, *J. Anal. Appl. Pyrolysis* **2014**, *110*, 254–263.
- [24] S. Patankar, *Numerical Heat Transfer and Fluid Flow*, Taylor & Francis, **1980**.
- [25] Webbook.nist.gov, **2016**.
- [26] T. L. Bergman, A. S. Lavigne, F. P. Incropera, D. P. Dewitt, *Fundamentals of Heat and Mass Transfer*, **2011**.
- [27] *Theoretical Manual Solidworks Simulation 2014*, Dassault Systemes, **2014**.
- [28] G. Lu, J. Wang, *Appl. Therm. Eng.* **2008**, *28*, 8–13.
- [29] S. Song, M. M. Yovanovich, K. Nho, *J. Thermophys. Heat Transf.* **1992**, *6*, 62–68.
- [30] S. R. Schmid, B. J. Hamrock, B. O. Jacobson, *Fundamentals of Machine Elements, Third Edition: SI Version*, Taylor & Francis, **2014**.
- [31] K. Nadolny, W. Kapłonek, *Meas. Sci. Rev.* **2014**, *14*, 204 – 212.
- [32] *Technical Reference: Solidworks Flow Simulation 2015*, Dassault Systemes, **2014**.
- [33] "Absolute Pipe Roughness," can be found under <http://www.efunda.com/formulae/fluids/roughness.cfm>, **2016**.
- [34] A. Erdemir, T. M. Guess, J. Halloran, S. C. Tadepalli, T. M. Morrison, *J. Biomech.* **2012**, *45*, 625–633.
- [35] W. M. Rohsenow, J. P. Hartnett, Y. I. Cho, *Handbook of Heat Transfer*, McGraw-Hill New York, **1998**.

FULL PAPER

Heat and mass transfer in a micropyrolysis system were studied both experimentally and computationally. These studies indicate that heating rates in micropyrolyzers are more modest than sometimes assumed and that diffusion from the interior of sample cups limited mass transfer rates when using intact deep cups. Use of a perforated shallow cup increased levoglucosan yields from pyrolysis of cellulose by 10%.



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**Heat and Mass Transfer Effects in a
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